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Molecular structure and paramagnetic properties of lantanides complexes with bisdiisobutil dithiophosphinate and 1,10-phenanthroline using NMR

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Magnetic Resonance Imaging (MRI) is routinely used in the clinic to visualize the structure and function of organs. For several applications, including tumor and cardiovascular imaging in clinic and *in vivo* studies, an enhancement in contrast is an absolute requirement to improve the sensitivity and the diagnostic contents of the images. For this, several contrast agents (CAs) have been developed over the past years, most of which incorporate paramagnetic gadolinium ions (Gd^{3+}). Currently, complexes of different lanthanides (Ln, other than Gd), remain largely unexplored as probes for nuclear magnetic resonance spectroscopy (NMR) and MRI.

The features of the molecular structure and paramagnetic properties of Ln complexes with the dithiophosphinate $R_2PS_2^-$ (R = *i*-Bu) and 1,10-phenanthroline ligands [Ln(1,10-Phen)((*i*-Bu)$_2$PS$_2$)$_2$(NO$_3$)] {where Ln = Nd^{3+} (I), Eu^{3+} (II), Dy^{3+} (III), Yb^{3+} (IV) and Lu^{3+} (V)} in $CDCl_3$ have been studied by ^{1}H NMR techniques. These complexes are of interest due to the prospect of using some of them as fluorescent sensors for biology and medicine. They are also considered as potential NMR thermometric probes (see our approach in [1, 2]). The structure of complexes was studied in detail by three independent ^{1}H NMR techniques that are analysis of lanthanide-induced shift (LIS) magnitudes, method of the separation of Fermi-contact and pseudo-contact contributions of LIS [3], and calculation of paramagnetic lanthanide-induced relaxation rate enhancements [2]. The structure results obtained for these paramagnetic complexes by relaxation spectroscopy (RS) of NMR and LIS analysis in solution are mutually consistent with the results found for model complex of yttrium by X-ray analysis in the crystalline phase. Paramagnetic complexes (I–IV) investigated in this work represent a new type of thermometric NMR sensors and lanthanide paramagnetic probes for *in situ* temperature control in solution. The report also contains: (1) comparison of the results obtained and those found for other Ln complexes; (2) the information about the molecular structure and the dynamics of related Ln coordination compounds with crown-ethers, (EDTA-like) ligands and DOTA-like molecules in solutions.

References

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